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CITATION:

NAGATA, Yoshinosuke ...[et al]. Polarographic Determination of the Rayon Pulp Ash (Part 1) : Calcium and Magnesium. 木材研究 : 京都大學木材研究所報告 1956, 16: 35-41

ISSUE DATE:

1956-07

URL:

http://hdl.handle.net/2433/52822

Polarographic Determination of the Rayon Pulp Ash (Part 1) Calcium and Magnesium

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(Recieved May 31, 1956)

Introduction

It has been recently discussed that, of the troubles in the rayon manufacture, the filtrability of the viscose was influenced by the organic substances as well as by the inorganic compounds. Further, it has been clarified that the exchange rate of nozzle caused by its clogg depended to some extent on the amounts of calcium in the pulp ash.

The quantitative determinations of calcium, which is the main component of the pulp ash, have been carried out by the many kinds of methods such as the gravimetric, volumetric, and colorimetric methods. And recently it has been determined by the complex titration with ethylenediamine tetraacetic acid (Complexone III)[1]. According to this method, however, calcium was titrated with magnesium together, since it was carried out without removal of magnesium. In the case of calcium determination in the pulp ash, the sum of calcium and magnesium were measured by the titration, and then the content of calcium was obtained by the calculation from the ratio of calcium to magnesium which was estimated by the other method beforehand.

In polarography, calcium does not show the reduction wave at the dropping mercury electrode in the usual electrolytic solution, so far as the special electrolyte such as tetramethyl ammonium bromide is not used as the supporting electrolyte[2]. Previously, it has been attempted to apply the indirect determination using chloranilinic acid[3] or picrolinic acid[4]. R. Pribil et al[5] carried out the calcium determination using Complexone III. We investigated the polarographic behaviors of the displacement reaction of calcium and magnesium with zinc complex of Complexone III. As the results of experiments, the separatory determination of calcium and magnesium could be carried out in the specific electrolytic solutions ; magnesium was removed as the precipitate by the addition of ammonium phosphate.

Experimental Part

Materials

Zinc-complex of Complexone III ; 1.90 gr. $ZnSO_4 \cdot 7H_2O$ and 2.48 gr. Complexone

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III are dissolved in 100 ml. of distilled water, and diluted to 1 liter with water and ammonia, the final concentration of which is about 12 N. Thus, the concentration of Zn-complex is 6.3×10^{-3} mol per liter.

2 N Ammonium chloride solution ; 1.08 gr. NH_4Cl is dissolved in 100 ml. water.

Saturated ammonium phosphate solution ; 40 gr. $(NH_4)_2HPO_4$ is dissolved in 100 ml. water.

Calcium oxide ; Calcium chloride in ammoniacal solution reacts with ammonium oxalate to form calcium oxalate. It is dissolved in dilute hydrochloric acid and reprecipitated with ammonium oxalate. Then it is ignited at 900°C to calcium oxide. Standard stock solution contains 10^{-2} M CaO.

Magnesium pyrophosphate ; Magnesium sulphate is precipitated as $MgNH_4PO_4$ with $(NH_4)_2HPO_4$ in ammoniacal solution. $MgNH_4PO_4$ is ignited to $Mg_2P_2O_7$ and 10^{-2} M $Mg_2P_2O_7$ solution is prepared as the standard solution.

Method

Yanagimoto pen-recording polarograph is used. The characteristic constant of the capillary used for the dropping mercury electrode is as follows ; the flow rate of mercury, m, and the drop time, t, at -1.5 V vs. Hg pool in the 0.2 N KCl solution are 1.936 mg/sec., and 3.56 sec., and hence $m^{2/3}t^{1/6}$ is 1.919 which is a constant in the Ilkovic equation $I_d=607nD^{1/2}Cm^{2/3}t^{1/6}$, where I_d, D and C denote the diffusion current, the diffusion coefficient and the concentration of the depolarizer, respectively. The mercury reservior lebel is usually 50 cm high except in the special case. Normal calomel electrode is used as the anode.

Experimental Results

I) Volume of Zinc-Complex Reagent to Be Added

Zn-complex of Complexone III reacts with the various cations such as Ca^{++}, Mg^{++}, Fe^{++}, Mn^{++}, etc., in the ammoniacal solution to form the complexone complex of these cations, to free zinc ion and to form Zn-ammon complex between freed Zn^{++} and ammonia according to equations (1) and (2).

$$M^{++}+\text{Zn-complex} \rightleftarrows Zn^{++}+\text{M-complex} \qquad (1)$$

$$Zn^{++}+6NH_3 \rightleftarrows Zn(NH_3)_6 \qquad (2)$$

The formed Zn-complex shows a so-called well-defined single reduction wave in the ammoniacal solution. This reaction proceeds rapidly and quantitatively. It is seen from Fig. 1 that 10 ml. of Zn-complex reagent in 25 ml. electrolytic solution is enough to displace 8×10^{-4} M Ca^{++} ion.

II) Relationship Between the Limiting Current and the Mercury Reservior Height

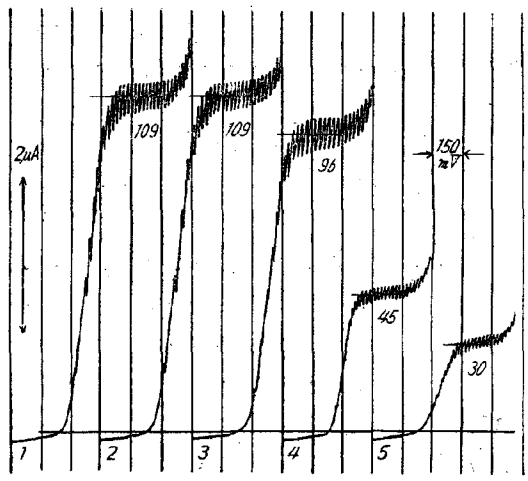


Fig. 1

Relationship between the Limiting Currents and the Amounts of Zn-complex Reagent. 2 ml. of 10^{-2} M Ca^{++} and 1 ml. of sat. $(NH_4)_2HPO_4$ in 25 ml. Temp.=25°C. Ml. of Zn-complex Reagent added: 1) 10, 2) 7.5, 3) 5.0, 4) 2.5, and 5) 0.

If the backward rate of the reaction according to eqs. (1) or (2) is sufficiently great, it is considered that the kinetic factor will be contained in the limiting current of Zn-complex. In the case of the diffusion current, the linearity exists between the current and the square root of the mercury reservior height (h)[6]. If, on the other hand, the kinetic factor is contained in the limiting current, the relation is different from the diffusion current ; i. e., in the typical case of the kinetic current, the current does not depend on the mercury reservior height[7]. It is known that the limiting current of Co^{++} reduction wave in 0.2N KCl solution is controlled by the diffusion process. Table 1 shows the relationship between the limiting current and the square root of the mercury reservior height under various conditions. The limiting current is directly proportional to $\sqrt{h}$ in all cases. This indicates, therefore, that the limiting current of these reduction waves in ammoniacal solutions are controlled by the diffusion process and do not contain the charactor of the so-called kinetic current.

Table 1
Dependence of the Limiting Current (i) on the Mercury Reservior Height (h)

h cm	$\sqrt{h}$	Mg	Ca			Co
		10 ml. Zn-complex Reagent			2 ml. Zn-complex Reagent	0.2 N KCl
		0.2 N NH_4Cl		None		
		i μA	i μA	i μA	i μA	i μA
80	8.94	5.44	6.92	5.52	2.76	2.72
70	8.37	5.02	6.40	5.16	2.16	2.52
60	7.70	4.72	6.00	4.76	1.96	2.36
50	7.07	4.32	5.48	4.36	1.80	2.16
40	6.32	3.88	4.96	3.84	1.60	1.92
30	5.48	3.32	4.24	3.32	1.40	1.64
Tangent at h=50		0.491	0.491	0.504	0.533	0.490

III) Removal of Magnesium

The main component in the pulp ash is calcium, beyond which magnesium,

iron, alminium, and manganese are contained. These metals except calcium and magnesium can be removed as the precipitate by the addition of ammonium hydroxide. Magnesium, however, is present with calcium in the solution even after the treatment. Hence, it is necessary to remove magnesium from the solution. After addition of Zn-complex reagent to the sample solution containing calcium and magnesium, saturated ammonium phosphate solution is added. As shown in Fig. 2, it is seen that the presence of magnesium does not interfere the wave height up to the same concentration as calcium. When present more, the wave height decreases resulting from the co-precipitation of calcium. Since magnesium in pulp ash is present below about a half of calcium, it seems proper to treat as above mentioned.

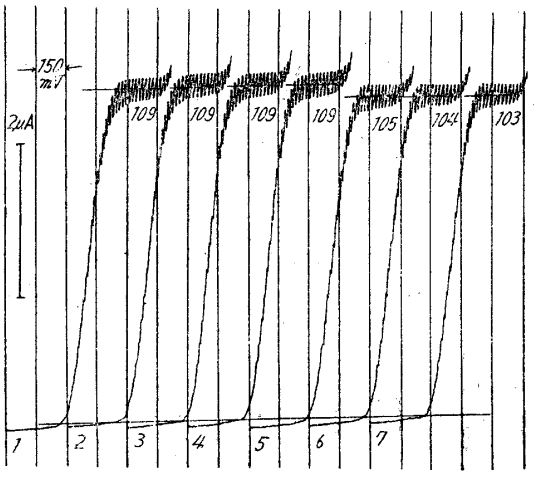


Fig. 2.

Influence of Mg^{++} on the Wave Heights. 2 ml. of 10^{-2} M Ca^{++}, 10 ml. of Zn-complex Reagnt and 1 ml. of Sat. $(NH_4)_2HPO_4$ in 25 ml. Temp = 25°C. Ml. of 10^{-2} M Mg^{++} solution added: 1) 0, 2) 0.2, 3) 0.5, 4) 1.0, 5) 2.0, 6) 3.0, and 7) 4.0.

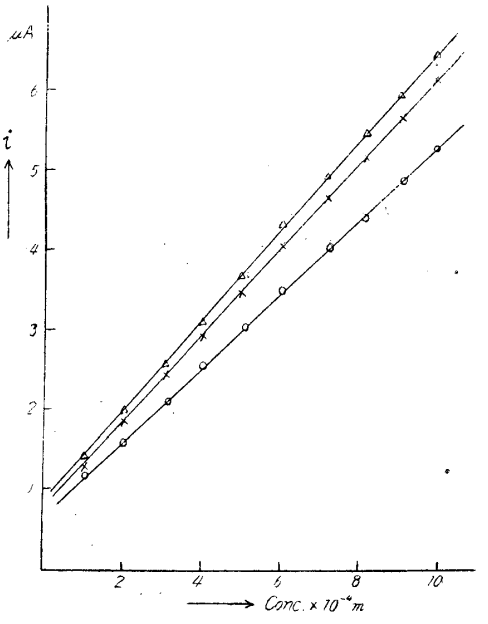


Fig. 3

Relationship between the Limiting Currents and the Concentrations of Ca^{++} and Mg^{++}. Temp. = 25° C. ○: Ca^{++} in $(NH_4)_2HPO_4$, ×: Ca^{++} in 0.2 N NH_4Cl, △: Mg^{++} in 0.2 N NH_4Cl.

On the other hand, when ammonium chloride instead of ammonium phosphate is used as the supporting electrolyte, the limiting current is due to the reduction of the total amount of zinc ion resulting from displacement of both calcium and magnesium.

IV) Relationship Between the Concentration and the Limiting Current

It is seen from Fig. 3 that the limiting currents are proportional to the concentration of calcium and magnesium under various conditions. These relationships are represented by the following equations according to the least square method.

1) Calcium in $(NH_4)_2 HPO_4$

$$i = 0.52 + 0.50C$$

2) Calcium in NH_4Cl

$$i = 0.83 + 0.52C$$

3) Magnesium in NH_4Cl

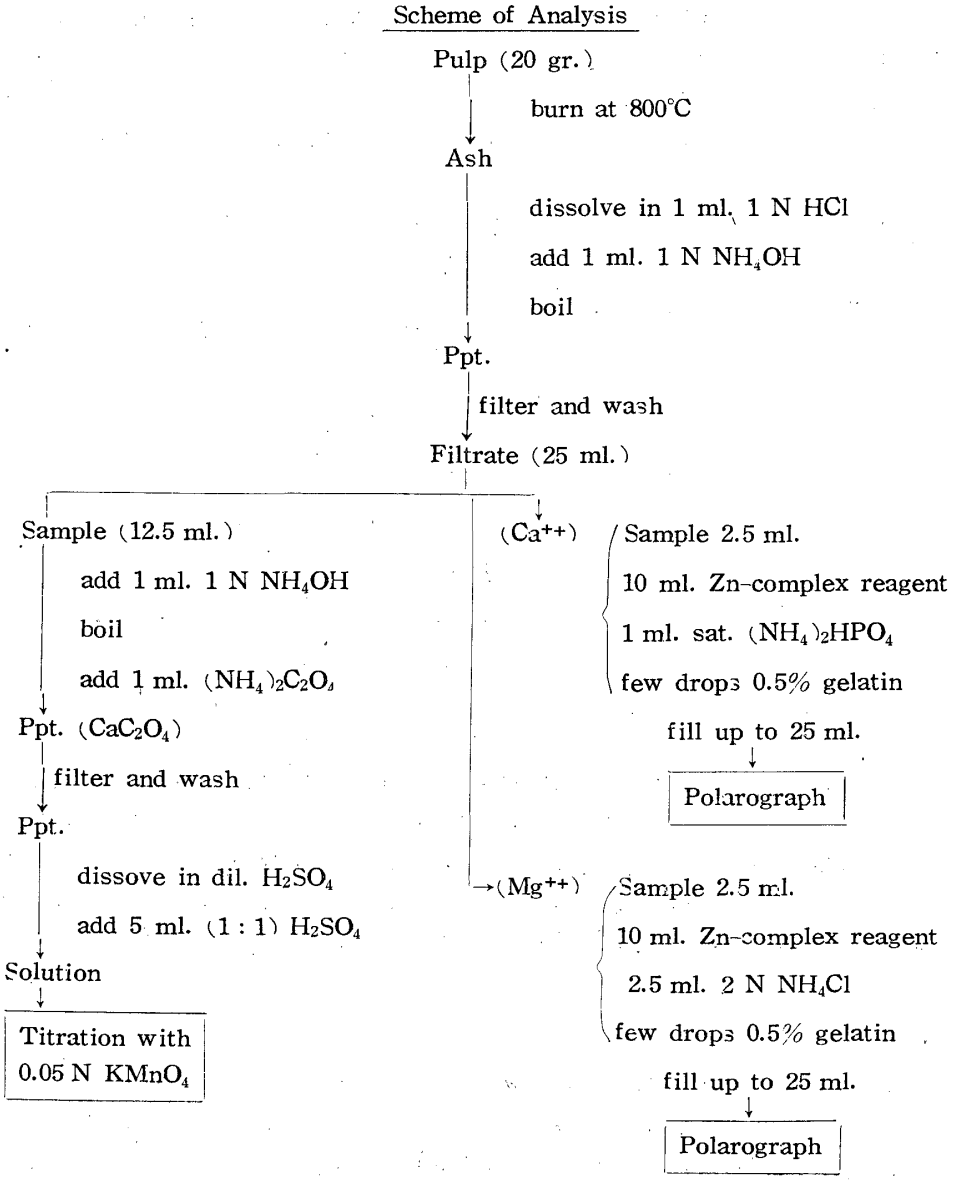
$$i = 0.87 + 0.57C$$

where i and C denote the limiting current in μA and the concentration of calcium or magnesium in 10^{-4} mol per liter, respectively. These three equations which represent the calibration curves, do not pass the zero point, because the limiting current is shown even in the blank solution, in which some amount of the free zinc ion is present.

V) Preparation of the Electrolytic Solutions

20 gr. of rayon pulp is ashed in the electric furnace at 800°C. The ash is dis-

Scheme of Analysis



solved in 1 ml. of 1 N HCl and neutralized by the addition of 1 ml. of 1 N NH_4OH solution. The produced precipitates are filtered off, and the volume of the filtrate and washing water is made to 25 ml. In the case of calcium determination, 10 ml. of Zn-complex reagent is added on a part of this sample solution, 2.5 ml., in 25 ml. mess flask, and 1 ml. of saturated $(NH_4)_2HPO_4$ solution and few drops of 0.5 % gelatin soulution are added, and filled up to the mark with distilled water. On the other hand, in the case of the total determination of calcium and magnesium, 2.5 ml. of 2 N NH_4Cl solution is added as the supporting electrolyte instead of $(NH_4)_2HPO_4$. These two electrolytic solutions are polarographed. The concentration of calcium is calculated according to eq. (3) from the former polarogram and that of magnesium is obtained by using eqs. (4) and (5) from both polarograms.

In order to compare the values measured polarographically with those determined by the other method, calcium is determined by the titration with potassium permanganate. 12.5 ml. of sample solution is made alkaline with ammonia, and 2 ml. of saturated $(NH_4)_2C_2O_4$ solution is added. The precipitate CaC_2O_4 is filtered, washed with water, dissolved in diluted H_2SO_4, and 5 ml. of 1 : 1 H_2SO_4 is added to the solution, and then the free oxalic acid is titrated with 0.05 N $KMnO_4$ solution.

Table 2

Pulp	Ash		CaO					MgO	
			Titr.		Polaro.		Difference	Polaro.	
	mg	% vs. Pulp	mg	% vs. Ash	mg	% vs. Ash	% vs. Titr.	mg	% vs. Ash
A	14.0	0.140	8.18	58.4	8.26	59.0	+0.9	2.93	20.9
B	9.5	0.095	4.68	49.3	4.76	50.1	+1.7	1.68	17.7
C	15.5	0.155	12.76	82.5	13.44	85.6	+3.5	0.805	5.19
D	8.3	0.083	4.83	58.2	4.90	59.6	+1.4	0.041	0.49
E	9.6	0.096	4.54	47.3	4.62	48.1	+1.8	0.415	4.32

Columns (6) and (4) in Table 2 represent the polarographic and volumetric values of calcium contents. It is seen from these results that a good agreement is shown between the polarographic and volumetric methods. We recommend the polarographic method for the separatory determination of calcium and magnesium, since this method is carried out far more repidly than the others and has same accuracy as the others.

Summary

Zinc-complex reagent is displaced with various cations to free zinc ion in the ammoniacal solution. The ammon-complex of this free zinc ion shows a reduction wave, the limiting current of which is controlled by the diffusion process and has a

linear relationship with the concentration of calcium or magnesium. Some interfering cations are removed by the suitable pre-treatment. As the supporting electrolyte, ammonium phoshate, which plays a role to precipitate magnesium, and ammonium chloride are used for the determination of calcium only and the total amounts of both, respectively. Each amount of calcium and magnesium is obtained by the calculation on the basis of the calibration equations. The polarographic results agree with the volumetric ones within 2% error.

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